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THE INHIBITING EFFECT OF SODIUM ETHYLENEDIAMINE TETRAACETATE ON THE AUTO-OXIDATION OF SODIUM SULFITE

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Annapolis, Maryland

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The Inhibiting Effect of Sodium
Ethylenediaminetetraacetate on
The Autoxidation of Sodium Sulfite

By

D. M. Zall

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ABSTRACT

The autoxidation of sodium sulfite (Na_2SO_3) is inhibited by disodium and tetrasodium ethylenediaminetetraacetate (EDTA). Results of experiments show that, when ions of copper and iron are chelated with EDTA, they no longer catalyze the oxidation of Na_2SO_3 . The effect of various concentrations of EDTA is also demonstrated.

Report MEL 172/67

ADMINISTRATIVE INFORMATION

The work reported here was performed under MEL Assignment 73 120, Sub-project S-F020 02 06, Task 0613.

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THE INHIBITING EFFECT OF SODIUM
ETHYLENEDIAMINETETRAACETATE ON
THE AUTOXIDATION OF SODIUM SULFITE

1.0 INTRODUCTION

In order to prevent waterside corrosion of steam generating plants used by the Navy, it is necessary to remove the dissolved oxygen from the water. In most cases this is accomplished by mechanical deaeration. When the efficiency of the deaerator is reduced, however, or when oxygen (air) leaks occur, it is necessary to supplement the oxygen-removal process with chemical treatment. Small amounts of oxygen can be scavenged economically by adding a reducing agent, such as sodium sulfite, to the feedwater. Theoretically, approximately 8 ppm* of sodium sulfite will react with 1 ppm of oxygen in the feedwater. An excess is used to compensate for the catalytic or autodecomposition of the sodium sulfite.

1.1 Background. A survey¹ of the technical literature covering sodium-sulfite reactions with dissolved oxygen and the catalytic effects of metal ion concentrations has been published. The oxidation of sodium sulfite is a first-order reaction with respect to both SO_3^{--} and O_2 concentration, according to Yagi and Inone,² who used a polarographic method for their investigation. They also studied the catalytic effect of the cobalt ion in promoting acceleration of the oxidation process. Cobalt promotes the process in proportion to its concentration. Copper ions also catalyze the decomposition or autoxidation of sodium sulfite, and, according to Bäckström, this is a chain reaction.^{3,4} In high concentrations, however, they have an inhibiting effect.

Brohm and Jain⁵ studied a number of organic compounds, such as tannin (1-percent solution), as inhibitors of the oxidation process. Other investigators⁶ observed that the presence of traces of certain organic compounds decrease the rate of oxygen removal. The inhibiting effect of ascorbic acid, however, was only satisfactory at pH 5. At a hydrogen-ion concentration

*Abbreviations used in this text are from the GPO Style Manual, 1959, unless otherwise noted.

¹Superscripts refer to similarly numbered entries in Appendix A.

greater than 5, and at increasing temperatures, however, the inhibiting effect was negligible. The present study was initiated to study the inhibiting effect of organic ions with compounds which have the additional property of being able to chelate the cations that promote oxidation of sodium sulfite.

1.2 Objective. The objective of this study was to increase the effectiveness of the use of sulfite as an oxygen scavenger in closed water systems. The chelating agent chosen was disodium ethylenediaminetetraacetate (Na_2EDTA). Other inhibitors were also included in some of the experiments.

2.0 PROCEDURES

While most experiments were conducted at ambient temperature (25 - 30 C), one experiment was performed by refluxing (boiling) the solution for 15 minutes. Distilled water with a maximum content of 8 ppm oxygen was used to prepare the 0.02N sodium-sulfite solutions (Na_2SO_3). Normally, the solutions were stored in glass stoppered flasks. In one of the experiments, however, the solutions were stored in polyethylene bottles. The flasks were opened only when a sample was withdrawn for the residual sulfite content, which was determined by titrating with potassium iodate (KIO_3) using starch as an indicator. The oxygen content was determined by the Winkler method.

In some of the experiments, additions of disodium phosphate (Na_2HPO_4) were made to simulate treated boiler water conditions and to determine the effect of change in pH. Various amounts (concentrations) of Na_2EDTA were added to the solutions to observe the effect. Solutions of Na_2SO_3 and Na_2HPO_4 of similar concentrations were used as controls. Copper-sulfate additions were made to some of the solutions to determine the catalytic effect of the copper ion on the instability of Na_2SO_3 and the effect of chelated copper when Na_2EDTA was added to the solution.

Iron chips were introduced into some of the sulfite solutions, simulating the effect of intimate contact of boiler water with the metallic environment. Other components, such as ferrous ammonium sulfate and nickel sulfate, were added to sulfite solutions to determine their effect. Reducing agents, such as ascorbic and oxalic acids, retarded the autoxidation of sodium sulfite.

3.0 RESULTS AND DISCUSSION

Results of experimental studies of the oxidation and autoxidation of sodium sulfite show the effects of catalysts and inhibitors on the chemical kinetics. Curve A of Figure 1 shows the rapid oxidation of Na_2SO_3 when air is bubbled through a solution containing 1250 ppm of the compound. Curve B shows a slower rate of oxidation when the solution is stored in a stoppered flask. Curve C shows an even slower rate of oxidation when the air in the solution has been replaced with nitrogen. Curves A and B of Figure 2 compare the effect of aeration and deaeration of a sodium sulfite solution before the addition of sodium sulfite. De-aeration has some retarding effect on the autoxidation of sodium sulfite.

The effect of phosphate on the stability of Na_2SO_3 is shown in Figure 3. Curves A and B are parallel and demonstrate the same rate of oxidation independent of the final pH value. The phosphate-sulfite solution ranges from an initial pH value of 9.5 to a final value of 9.3. The sulfite solution alone, however, ranges from an initial pH value of 9.3 to a final value of 6.9.

3.1 Additions. The addition of ascorbic acid to sodium-sulfite solutions inhibited its oxidation. Curves A, B and C of Figure 4 show the effect of three different concentrations of ascorbic acid in Na_2SO_3 solutions. A concentration of 25 ppm was more effective than 10 ppm, but not quite as effective as 50 ppm. The pH of the solutions ranged from 5.0 to 5.2. Neither oxalic acid nor ferrous-ammonium sulfate, however, was an effective inhibitor, as shown in Figures 4 and 5. Of the three reducing agents, only ascorbic acid is capable of breaking the reaction chain, thus effecting inhibition. In the case of ferrous-ammonium sulfate, the product (ferric-ammonium sulfate) catalyzes the autoxidation and nullifies the reducing action of its parent compound. When this product is chelated, as shown in Figure 5, Curve B, the inhibition action of the reducing agent is apparent. Due to the stability of oxalic acid and its resistance to oxidation at ambient temperature, it is not expected to inhibit the oxidation of sodium sulfite, since breaking of the chain occurs only as the inhibitor is oxidized. The contact of the sodium-sulfite solution with metallic surfaces (such as iron chips, Figure 6, Curve A) does not result in either acceleration or

inhibition of autoxidation. When a chelating agent (such as disodium EDTA) is added, retardation of oxidation occurs as shown in Figure 6, Curve B.

The addition of EDTA to a sodium-sulfite solution retards and inhibits its autoxidation. Figure 7 shows the effect of the addition of 10 ppm of Na_2EDTA . Whether aerated or not, the effect is the same. Figure 8 illustrates the inhibiting effect of autoxidation. After a rapid oxidation of Na_2SO_3 , the process of oxidation was stopped as soon as 20 ppm of Na_2EDTA was added to the Na_2SO_3 solution. Smaller concentrations of EDTA are not as effective as indicated by Curve A of Figure 9. Additions of 1 to 4 ppm, however, have the same retarding effect. Figure 9 illustrates the effect of various concentrations of the EDTA and the effect of deaeration. Curve D shows that, when the Na_2SO_3 solution was deaerated, much less of the Na_2SO_3 was autoxidized. Refluxing the solution (heated to 100 C) for 15 minutes did not destroy the inhibitor, since it had no appreciable effect on the inhibiting power of the EDTA.

3.2 Copper Effects. The addition of copper ions to the Na_2SO_3 solution (0.7 to 20 ppm) did not appreciably effect the autoxidation mechanism. This is not in contradiction to the observations of Kobe and Gooding⁷ or of Wickert and Ipach,⁸ who found greatly accelerated decomposition in the presence of copper ions. In their experiments, the solution was continuously exposed to the atmosphere. Figure 10 shows that the oxidation of the Na_2SO_3 solution was not effected by the concentration of the copper in the range of 0.7 to 20 ppm. The oxidation was essentially the same. Figure 11 shows that additions of EDTA altered the oxidation mechanism. When the ratio of copper to EDTA was 1 to 1, some inhibition occurred. When the ratio of copper to EDTA was 1 to 5, inhibition was marked.

4.0 CONCLUSIONS

The inhibiting effect of disodium EDTA on the oxidation of sodium sulfite has been demonstrated. It is effective even in the presence of cations, such as iron and copper.

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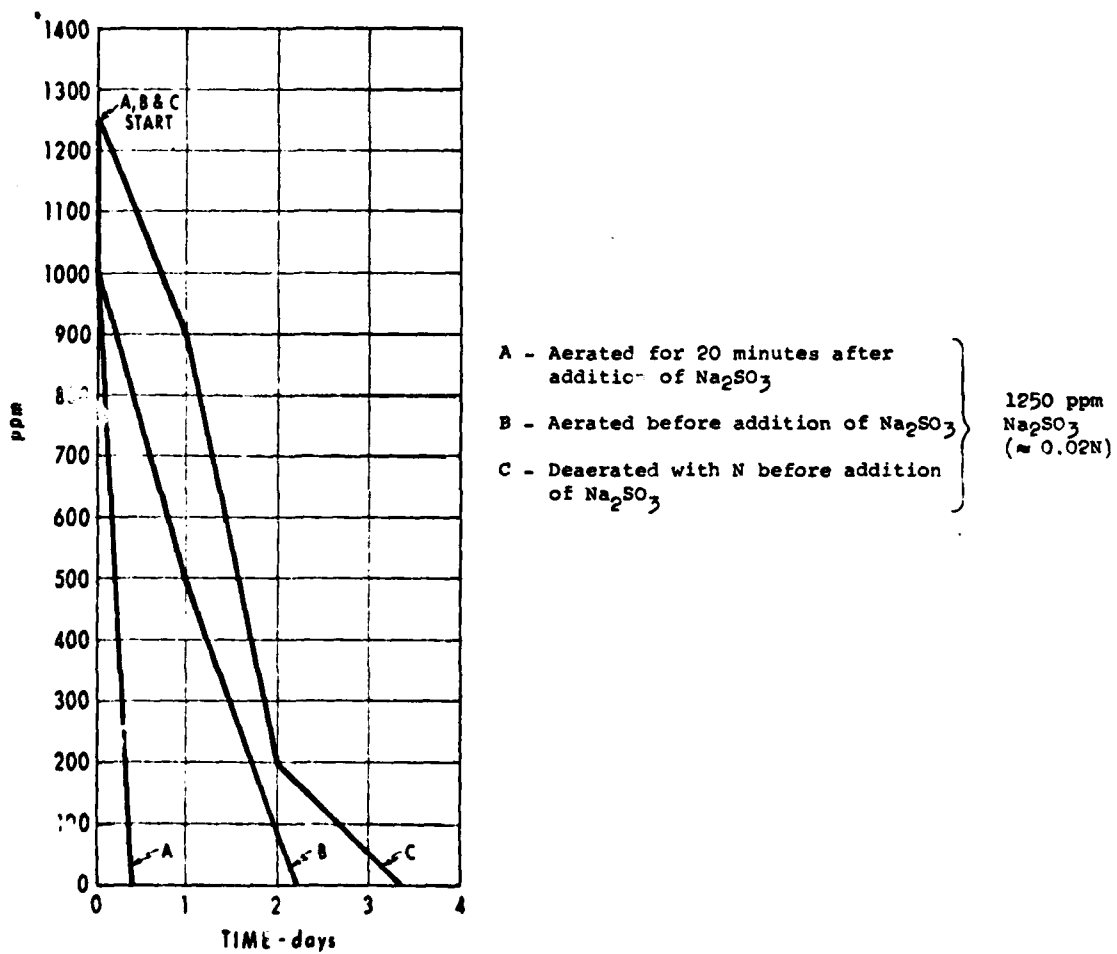


Figure 1

Effect of Oxygen on Na_2SO_3 Solutions

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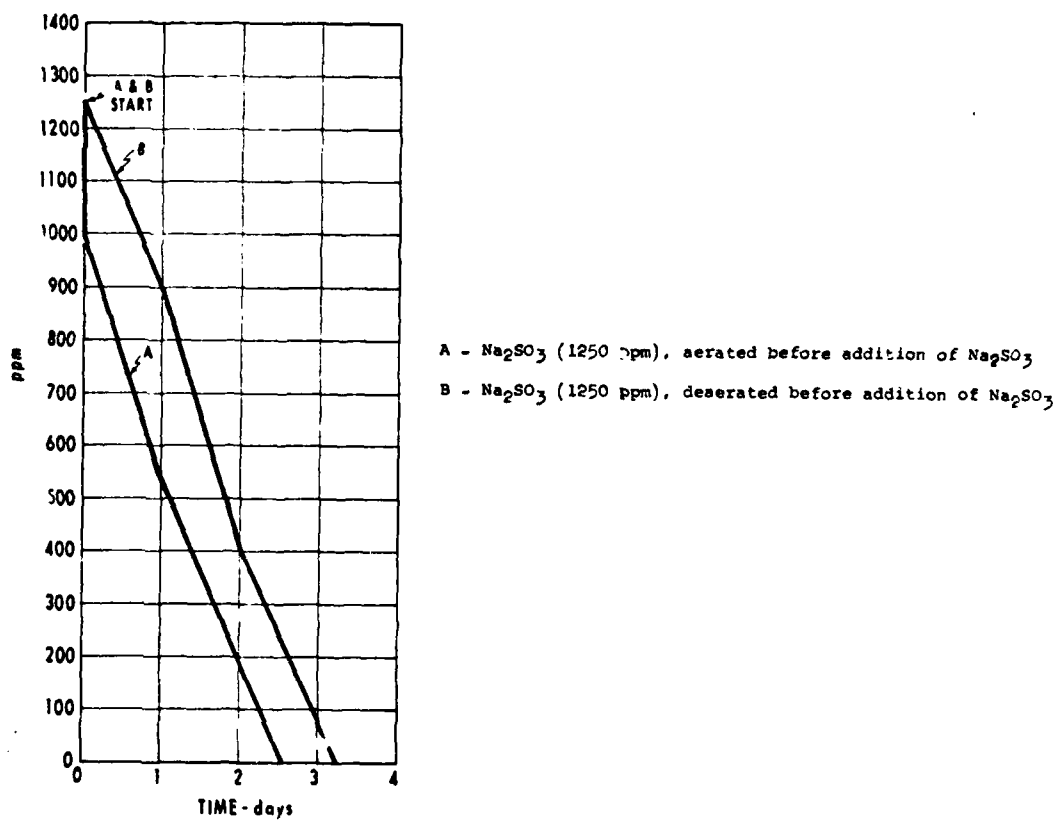


Figure 2

Effect of Deaeration of Na_2SO_3 Solutions

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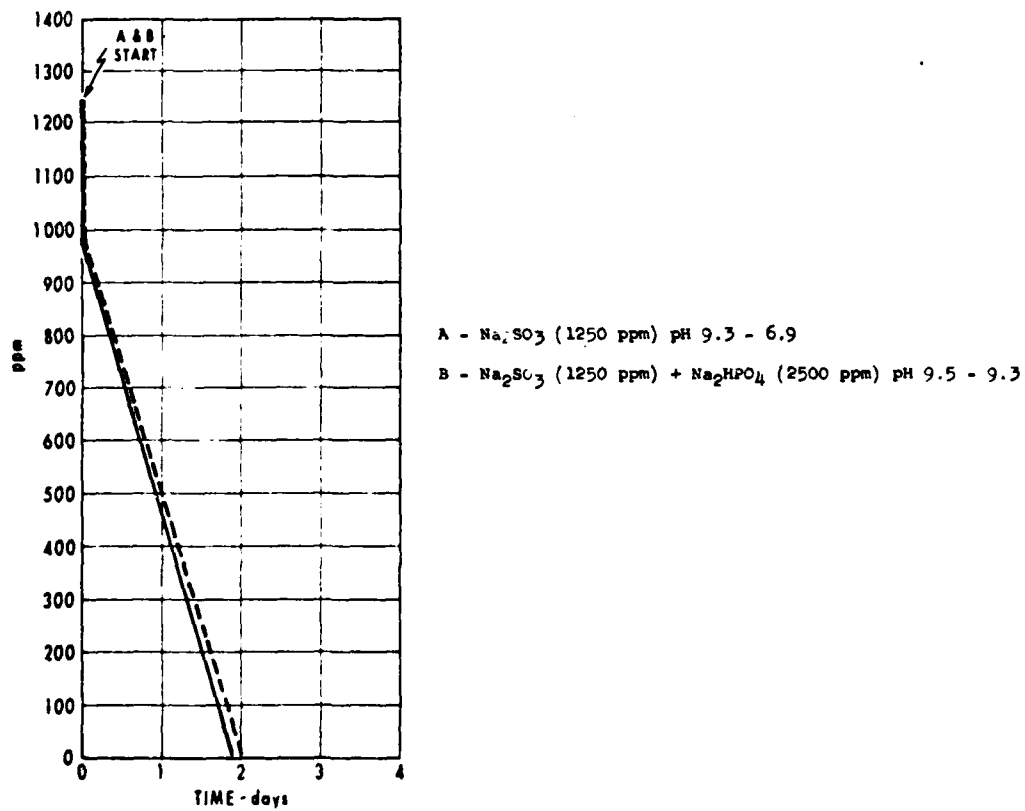


Figure 3

Effect of pH and Phosphate

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- A - $\left\{ \begin{array}{l} 1.25 \text{ g Na}_2\text{SO}_3 \\ 2.50 \text{ g Na}_2\text{HPO}_4 \\ 0.01 \text{ g ascorbic acid} \end{array} \right\}$ Liter
- B - $\left\{ \begin{array}{l} 1.75 \text{ g Na}_2\text{SO}_3 \\ 2.50 \text{ g Na}_2\text{HPO}_4 \\ 0.025 \text{ g ascorbic acid} \end{array} \right\}$ Liter
- C - $\left\{ \begin{array}{l} 1.25 \text{ g Na}_2\text{SO}_3 \\ 2.50 \text{ g Na}_2\text{HPO}_4 \\ 0.05 \text{ g ascorbic acid} \end{array} \right\}$ Liter
- D - $\left\{ \begin{array}{l} 1.25 \text{ g Na}_2\text{SO}_3 \\ 2.50 \text{ g Na}_2\text{HPO}_4 \\ 0.40 \text{ g oxalic acid (COOH)} \end{array} \right\}$ Liter

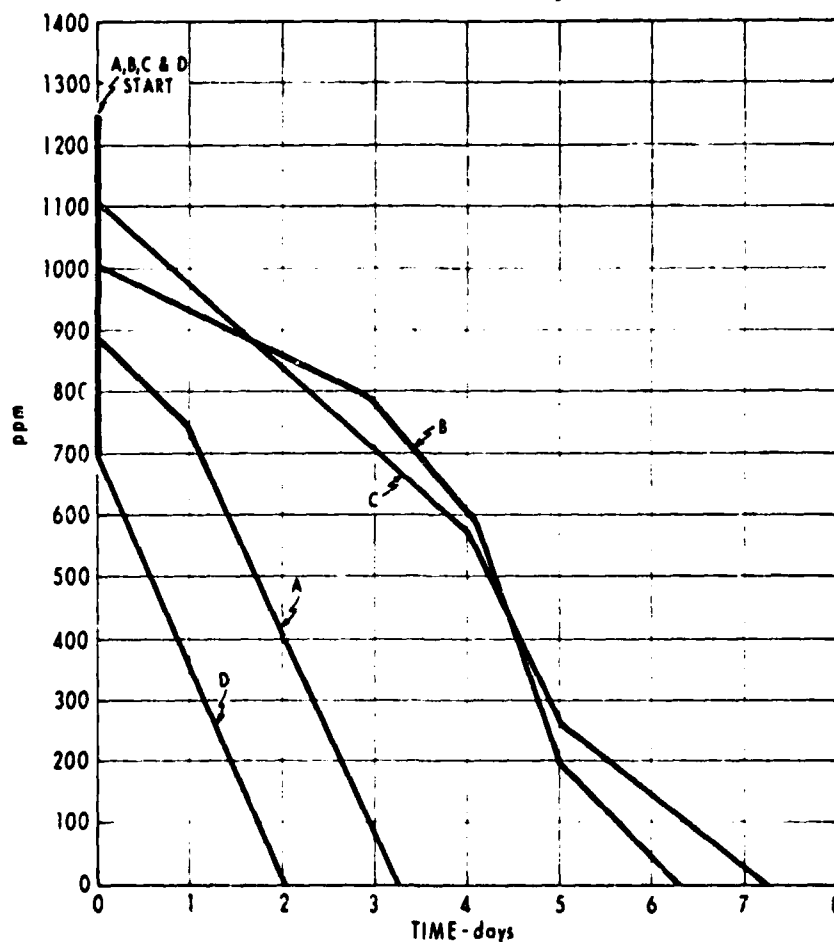


Figure 4 - Addition of Ascorbic and Oxalic Acids

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A - $\left\{ \begin{array}{l} 1.25 \text{ g Na}_2\text{SO}_3 \\ 2.50 \text{ g Na}_2\text{HPO}_4 \\ 0.40 \text{ g Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \end{array} \right\}$ Liter

B - $\left\{ \begin{array}{l} 1.25 \text{ g Na}_2\text{SO}_3 \\ 2.50 \text{ g Na}_2\text{HPO}_4 \\ 0.40 \text{ g Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \\ 0.40 \text{ g Na}_2\text{EDTA} \end{array} \right\}$ Liter

C - $\left\{ \begin{array}{l} 1.25 \text{ g Na}_2\text{SO}_3 \\ 0.01 \text{ g NiSO}_4 \end{array} \right\}$ Liter

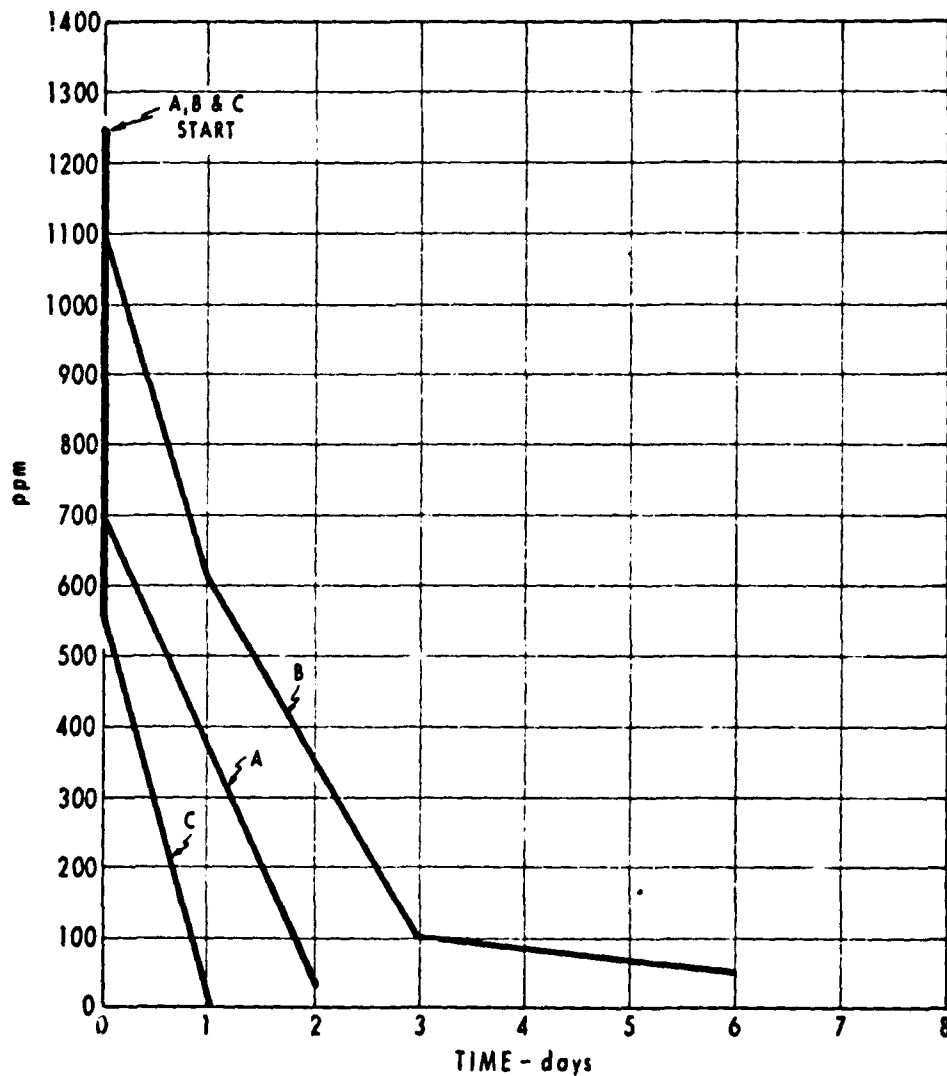


Figure 5 - Iron and Nickel Additions

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A - 1.25 g Na_2SO_3 } + 1 g iron chips
B - 1.25 g Na_2SO_3 } Liter + 1 g iron chips + 20 ppm Na_2EDTA

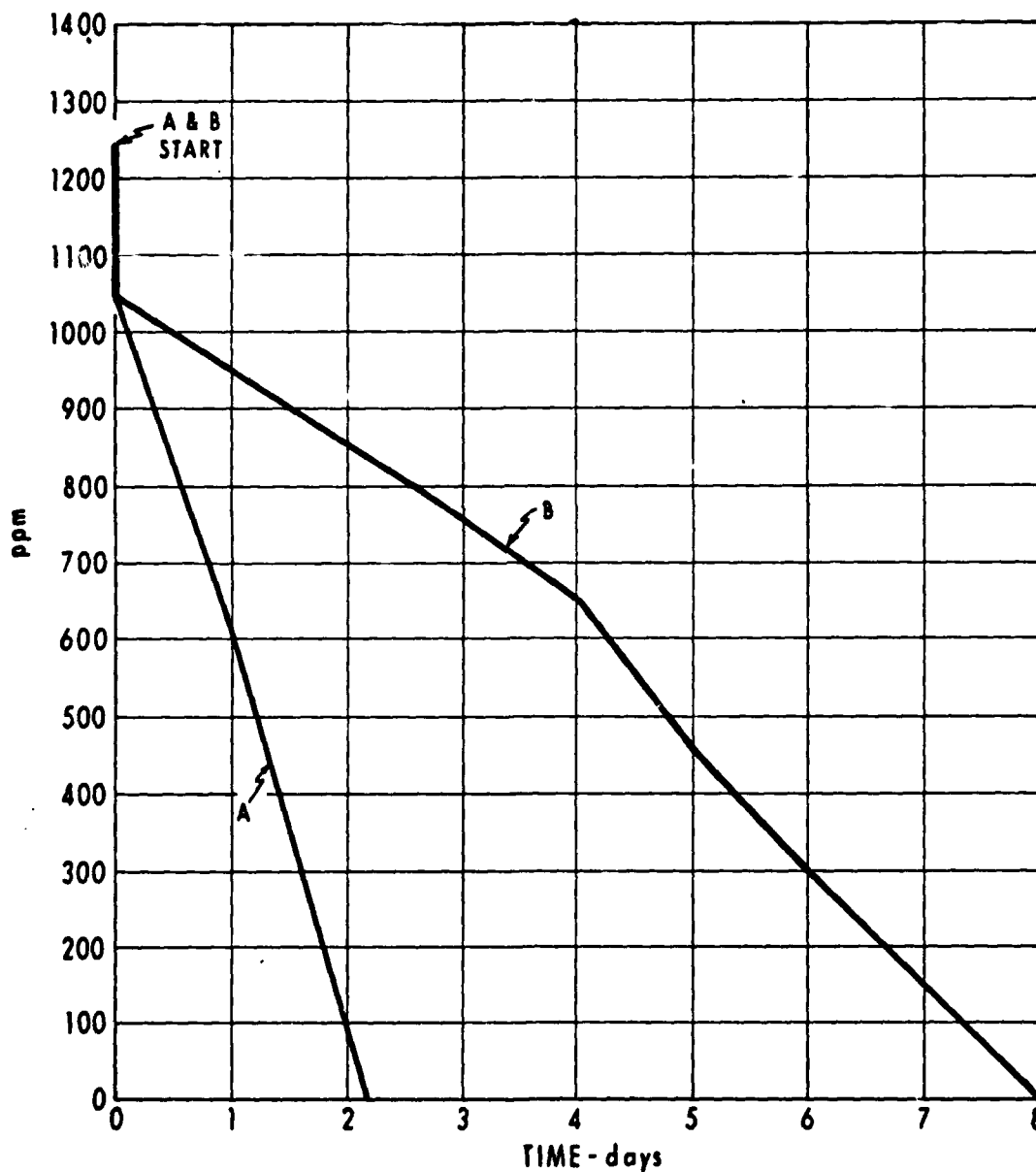


Figure 6 - Metal Contact vs EDTA

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1250 ppm Na_2SO_3 + 10 ppm Na_2EDTA

A - Aerated before addition of Na_2SO_3 and Na_2EDTA

B - Not aerated

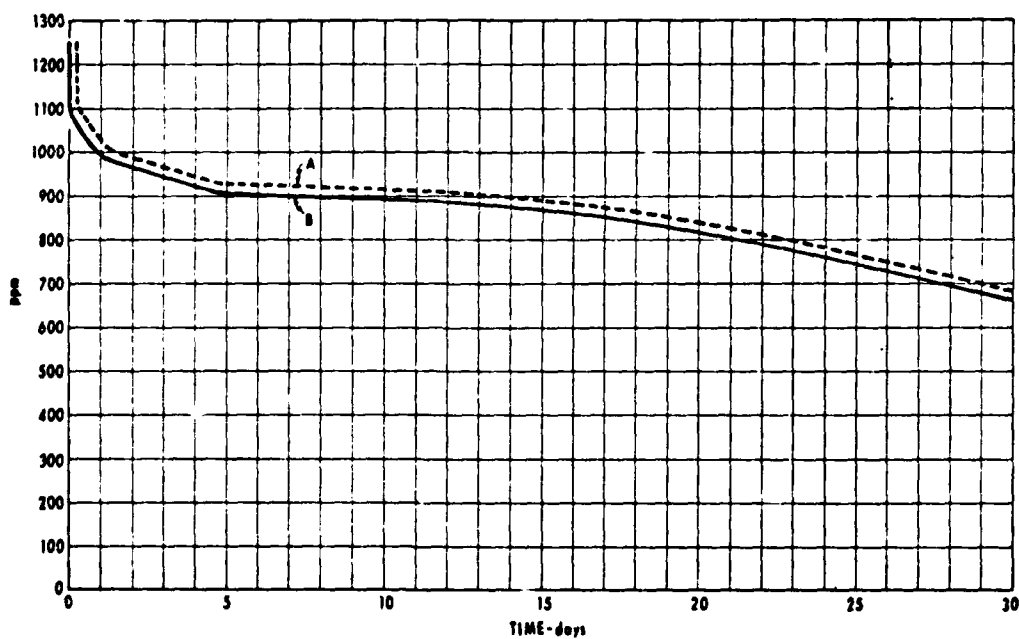


Figure 7

Aeration

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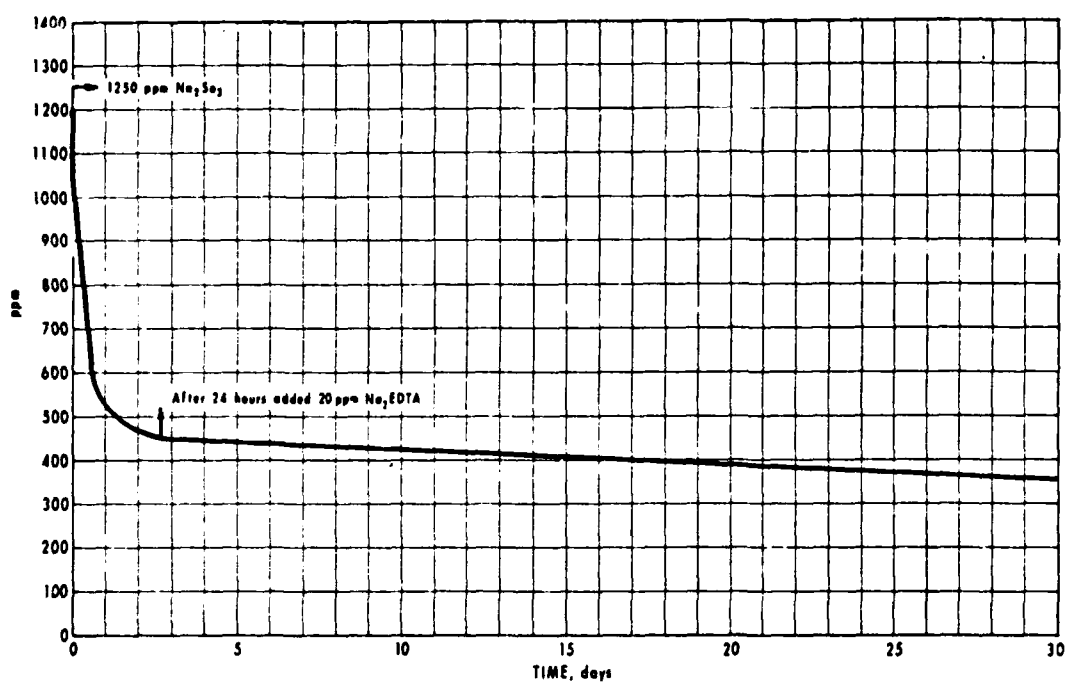


Figure 8

Effect of EDTA

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- | | | |
|--|---|-------|
| <p>A - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 + 1.0 ppm Na_2EDTA</p> <p>B - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 + 2.0 ppm Na_2EDTA</p> <p>C - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 + 40-100 ppm Na_2EDTA</p> <p>D - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 + 20 ppm Na_2EDTA
(deaerated with N)</p> <p>E - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 + 20 ppm Na_2EDTA
(refluxed for 15 minutes)</p> | } | Liter |
|--|---|-------|

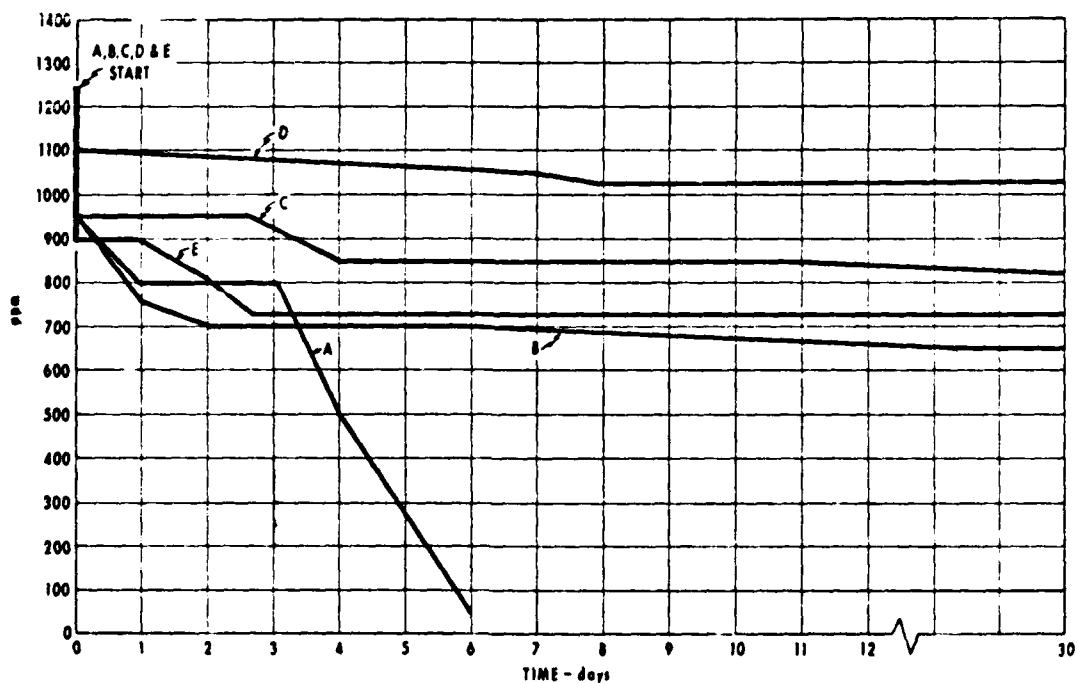


Figure 9

Various Concentrations of EDTA

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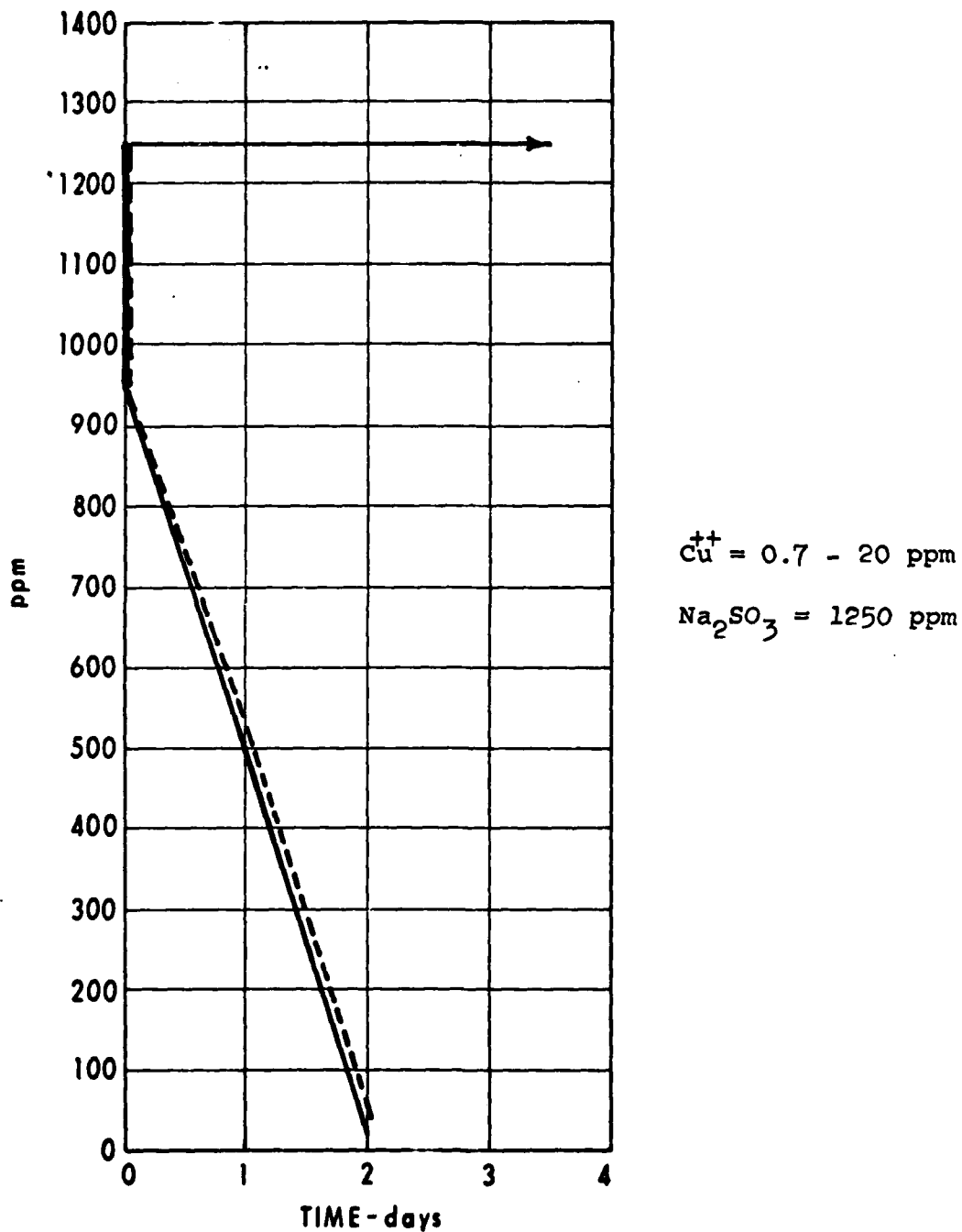


Figure 10

Additions of Copper Ions

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A - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 } + (Cu^{++} + Na EDTA), Ratio $\frac{\text{Cu}}{\text{EDTA}} \frac{1}{1}$
 B - 1.25 g Na_2SO_3 + 2.5 g Na_2HPO_4 } Liter + (Cu^{++} + Na EDTA), Ratio $\frac{\text{Cu}}{\text{EDTA}} \frac{1}{5}$

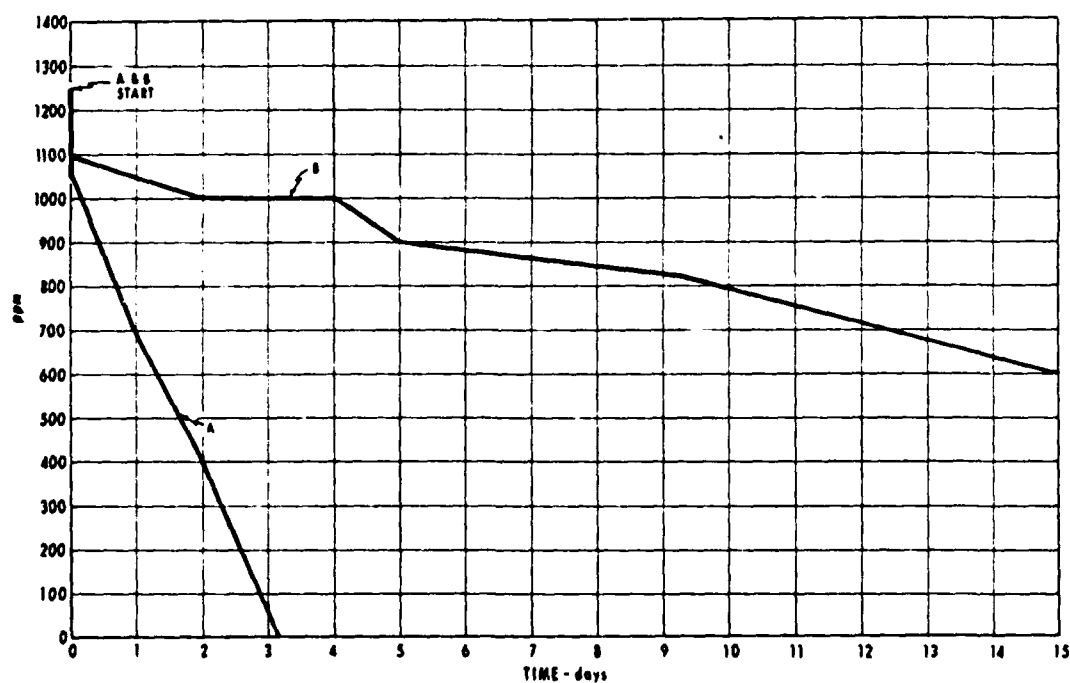


Figure 11

Copper Ions vs EDTA

Appendix A

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